

# **The General Phase Behavior of Ionic Liquids 1-Alkyl-3-methylimidazonium-bis(trifluoromethylsulfonyl)amides ( $C_n\text{mimNTf}_2$ ) with $n$ -Alkyl Alcohols ( $C_n\text{OH}$ )**

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The knowledge of thermodynamic properties like the solubilities or more generally phase-diagrams of Ionic Liquids (ILs) is a prerequisite for their application as, e.g., catalysts, reaction or extraction media. A large number of studies dealing with the physico-chemical characterization of IL systems can be found in the literature, but systematic studies focusing on solubilities or the partial miscibility are still rare. To this end we have studied the liquid-liquid (LLE) phase behavior of mixtures of different 1-alkyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)amides ( $C_x\text{mimNTf}_2$ ;  $2 \leq x \leq 12$ ) with  $n$ -alkyl alcohols ( $C_n\text{OH}$ ;  $3 \leq n \leq 20$ ). Applying the cloud point method the LLEs were determined in a temperature range of 275 – 423 K at ambient pressure. Partial miscibility with upper critical solution temperatures (UCST) is observed showing a rising trend with increasing chain lengths of the alcohols. A numerical analysis of the phase diagrams presuming Ising criticality is performed. Concepts for the description of the asymmetry of the phase diagram presuming the validity of the rectilinear diameter rule or a non-linear diameter requested by the theory of complete scaling are applied. The systematic trends of the phase behavior and the results of the analysis (UCST, critical composition, width and diameter of the phase diagrams) are discussed in detail. The large number of single systems investigated allows for a more general view at the results. The application of corresponding phase behavior on the systems investigated so far yields one single master-curve for more than 45 single systems. Furthermore a simple empirical relationship is formulated which allows for the description or estimate of UCSTs of the IL-alcohol family with an accuracy of about 10 K taking the ratio of the molar volumes of the alcohol and the 1-alkyl-3-methylimidazolium cation of the ionic liquid into account.